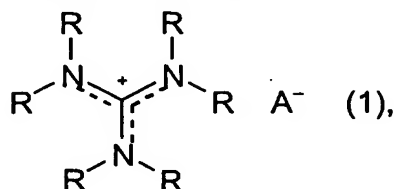


Patent Claims

1. Process for the preparation of guanidinium salts of the formula (1)

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in which the substituents R in each case, independently of one another, have the meaning of hydrogen,

straight-chain or branched alkyl having 1-20 C atoms,

saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms,

which may be substituted by alkyl groups having 1-6 C atoms,

15

where one or more substituents R may be partially or fully substituted by halogen or partially by CN or NO₂ and halogen denotes F, Cl, Br or I, where up to four substituents R may be bonded to one another in pairs by a single or double bond

20

and where a carbon atom or two non-adjacent carbon atoms of one or more substituents R may be replaced by atoms and/or atom groups selected from the group -O-, -C(O)-, -C(O)O-, -S-, -S(O)-, -SO₂-, -SO₃-, -N=, -N=N-, -NH-, -NR'-, -PR'-, -P(O)R'-, -P(O)R'-O-, -O-P(O)R'-O-, and -P(R')₂=N-, where R' denotes non-fluorinated, partially or perfluorinated alkyl having 1-6 C atoms, saturated or partially unsaturated cycloalkyl having 3-7 C atoms, unsubstituted or substituted phenyl or an unsubstituted or substituted heterocycle

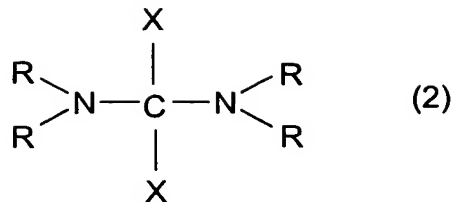
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and

A⁻ is a sulfonate, alkyl- or arylsulfate, hydrogensulfate, imide, methanide, carboxylate, phosphate, phosphinate, phosphonate, borate, thiocyanate, perchlorate, fluorosilicate or nitrate,

30

by reaction of a compound of the formula (2)



5

in which the substituents R have a meaning indicated for formula (1) and X denotes F, Cl or Br,

with a compound of the formula (3)

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in which A⁻ has a meaning indicated for formula (1) and

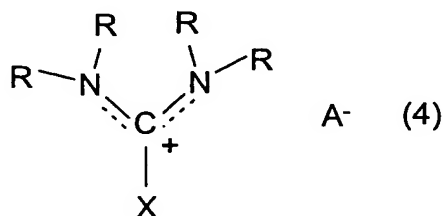
Kt⁺ can be a proton, R''₃Si, an alkali or alkaline earth metal cation, an ammonium cation, a phosphonium cation or a cation from group 11 or 12,

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where R'' in each case, independently of one another, denotes phenyl or a linear or branched alkyl group having 1-6 C atoms, which may be substituted by phenyl,

and subsequent reaction of the resultant compound of the formula (4)

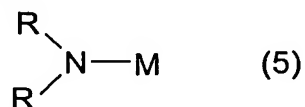
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where the substituents R, X and A⁻ have a meaning indicated for formula (1) or (2),

25

with compounds of the formula (5)



30

where the substituents R have a meaning indicated for formula (1) and M denotes hydrogen, R''₃Si, an alkali or alkaline earth metal and

R'' in each case, independently of one another, denotes phenyl or a linear or branched alkyl group having 1-6 C atoms, which may be substituted by phenyl.

- 5 2. Process according to Claim 1, characterised in that compounds of the formula $Kt^+ A^-$ (3) are employed, in which Kt^+ has a meaning indicated in Claim 1 and

A^- is selected from the group

- 10 $[R^1OSO_3]^-$, $[R^1SO_3]^-$, $[R^F SO_3]^-$, $[(FSO_2)_2N]^-$, $[(R^F SO_2)_2N]^-$,
 $[(R^F SO_2)(R^F CO)N]^-$, $[(R^F SO_2)_3C]^-$, $[(FSO_2)_3C]^-$, $[R^1CH_2C(O)O]^-$,
 $[R^F C(O)O]^-$, $[P(C_n F_{2n+1-m} H_m)_y F_{6-y}]^-$, $[P(C_6 F_5)_y F_{6-y}]^-$, $[(R^1 O)_2 P(O)O]^-$,
 $[R^1_2 P(O)O]^-$, $[R^1 P(O)O_2]^{2-}$, $[R^F_2 P(O)O]^-$, $[R^F P(O)O_2]^{2-}$, $[BF_{4-z} R^F_z]^-$,
 $[BF_{4-z} (CN)_z]^-$, $[B(C_6 F_5)_4]^-$, $[B(OR^1)_4]^-$, $[N(CN)_2]^-$, $[C(CN)_3]^-$, $[N(CF_3)_2]^-$,
 $[HSO_4]^-$, $[SiF_6]^{2-}$, $[ClO_4]^-$, $[SCN]^-$ and $[NO_3]^-$,

- 15 in which the substituents R^F in each case, independently of one another, have the meaning of

perfluorinated and straight-chain or branched alkyl having 1-20 C atoms, perfluorinated and straight-chain or branched alkenyl having 2-20 C atoms and one or more double bonds,

- 20 perfluorinated and saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms, which may be substituted by perfluoroalkyl groups, where the substituents R^F may be bonded to one another in pairs by a single or double bond and

- 25 where a carbon atom or two non-adjacent carbon atoms of the substituent R^F which are not in the α -position to the heteroatom may be replaced by atoms and/or atom groups selected from the group -O-, -C(O)-, -S-, -S(O)-, -SO₂-, -N=, -N=N-, -NR'-, -PR'- and -P(O)R'-, where R' denotes non-fluorinated, partially or perfluorinated alkyl having 1-6 C atoms, saturated or partially unsaturated cycloalkyl having 3-7 C atoms,
 30 unsubstituted or substituted phenyl or an unsubstituted or substituted heterocycle,

in which the substituents R^1 in each case, independently of one another, have the meaning of

straight-chain or branched alkyl having 1-20 C atoms,

5 straight-chain or branched alkenyl having 2-20 C atoms and one or more double bonds,

straight-chain or branched alkynyl having 2-20 C atoms and one or more triple bonds,

10 saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms, which may be substituted by alkyl groups having 1-6 C atoms,

where the substituents R^1 may be partially substituted by CN, NO_2 or halogen and

halogen denotes F, Cl, Br or I,

15 where the substituents R^1 may be bonded to one another in pairs by a single or double bond and

where a carbon atom or two non-adjacent carbon atoms of the substituent R^1 which are not in the α -position to the heteroatom may be replaced by atoms and/or atom groups selected from the group -O-, -C(O)-,

20 -C(O)O-, -S-, -S(O)-, -SO₂-, -SO₃-, -N=, -N=N-, -NH-, -NR'-, -PR'-, -P(O)R'-, P(O)R'O-, OP(O)R'O-, -PR'₂=N-, -C(O)NH-, -C(O)NR'-, -SO₂NH- or -SO₂NR'-, where R' denotes non-fluorinated, partially or perfluorinated alkyl having 1-6 C atoms, saturated or partially unsaturated cycloalkyl having 3-7 C atoms, unsubstituted or substituted phenyl or an unsubstituted or substituted heterocycle

25 and the variables

n denotes 1 to 20,

m denotes 0, 1, 2 or 3,

y denotes 0, 1, 2, 3 or 4, and

30 z denotes 0, 1, 2, 3 or 4.

3. Process according to Claim 1 or 2, characterised in that A⁻ is selected from the group

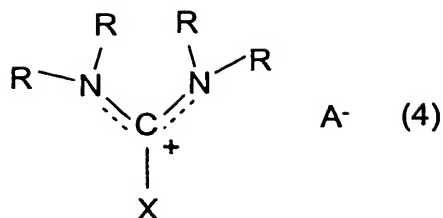
[CH₃OSO₃]⁻, [C₂H₅OSO₃]⁻, [C(CN)₃]⁻,
 [CH₃SO₃]⁻, [C₈H₁₇SO₃]⁻, [CH₃C₆H₄SO₃]⁻, [CF₃SO₃]⁻, [C₂H₅SO₃]⁻,
 5 [CF₃CF₂SO₃]⁻, [(CF₃SO₂)₂N]⁻, [(FSO₂)₂N]⁻, [(CF₃SO₂)(CF₃CO)N]⁻,
 [(C₂F₅SO₂)(CF₃CO)N]⁻, [(C₂F₅SO₂)₂N]⁻, [(CF₃SO₂)₃C]⁻, [(C₂F₅SO₂)₃C]⁻,
 [(FSO₂)₃C]⁻, [CH₃C(O)O]⁻, [C₂H₅C(O)O]⁻, [CF₃C(O)O]⁻,
 [CF₃CF₂C(O)O]⁻, [PF₆]⁻, [P(C₂F₅)₃F₃]⁻, [P(C₄F₉)₃F₃]⁻, [P(CF₃)₃F₃]⁻,
 [P(C₂F₄H)(CF₃)₂F₃]⁻, [P(C₂F₃H₂)₃F₃]⁻, [P(C₂F₅)(CF₃)₂F₃]⁻, [P(C₆F₅)₃F₃]⁻,
 10 [P(C₃F₇)₃F₃]⁻, [P(C₂F₅)₂F₄]⁻, [(HO)₂P(O)O]⁻, [(CH₃O)₂P(O)O]⁻,
 [(C₂H₅O)₂P(O)O]⁻, [(C₂F₅)₂P(O)O]⁻, [(C₂F₅)P(O)O₂]²⁻, [P(C₆F₅)₂F₄]⁻,
 [(CH₃)₂P(O)O]⁻, [CH₃P(O)O₂]²⁻, [(CF₃)₂P(O)O]⁻, [CF₃P(O)O₂]²⁻, [BF₄]⁻,
 [BF₃(CF₃)]⁻, [BF₂(C₂F₅)₂]⁻, [BF₃(C₂F₅)]⁻, [BF₂(CF₃)₂]⁻, [B(C₂F₅)₄]⁻,
 [BF₃(CN)]⁻, [BF₂(CN)₂]⁻, [B(CN)₄]⁻, [B(OCH₃)₄]⁻, [B(CF₃)₄]⁻,
 15 [B(OCH₃)₂(OC₂H₅)₂]⁻, [B(O₂C₂H₄)₂]⁻, [B(O₂C₂H₂)₂]⁻, [B(O₂C₆H₄)₂]⁻,
 [N(CN)₂]⁻, [N(CF₃)₂]⁻, [HSO₄]⁻, [ClO₄]⁻, [SiF₆]⁻, [SCN]⁻ or [NO₃]⁻.

4. Process according to one or more of Claims 1 to 3, characterised in that the substituent X in dihalogen compounds of the formula (2) according to Claim 1 denotes fluorine or chlorine.

5. Process according to one or more of Claims 1 to 4, characterised in that the substituent R in compounds of the formula (5) according to Claim 1 in each case, independently of one another, has the meaning of hydrogen,
 25 straight-chain or branched alkyl having 1-20 C atoms or saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms, which may be substituted by alkyl groups having 1-6 C atoms.

6. Process according to one or more of Claims 1 to 5, characterised in that the first step of the process is carried out in water.

7. Process according to one or more of Claims 1 to 6, characterised in that the first step of the process is carried out at temperatures of 0° to 150°C.
- 5 8. Process according to one or more of Claims 1 to 5, characterised in that the first step of the process is carried out in an organic solvent.
9. Process according to one or more of Claims 1 to 5 and 8, characterised in that the first step of the process is carried out at temperatures of -50° to 150°C.
- 10 10. Process according to one or more of Claims 1 to 9, characterised in that the second step of the process is carried out without a solvent.
11. Process according to one or more of Claims 1 to 10, characterised in that the second step of the process is carried out at a temperature at which at least one component is liquid.
- 15 12. Process according to one or more of Claims 1 to 9, characterised in that the second step of the process is carried out in an organic solvent.
- 20 13. Process according to one or more of Claims 1 to 9 and 12, characterised in that the second step of the process is carried out at temperatures of -50° to 150°C.
- 25 14. Process according to one or more of Claims 1 to 9, characterised in that the second step of the process is carried out in water.
15. Process according to one or more of Claims 1 to 9 and 14, characterised in that the second step of the process is carried out at temperatures of 0° to 150°C.
- 30 16. Compounds of the formula (4)



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in which the substituents R in each case, independently of one another, have the meaning of hydrogen, straight-chain or branched alkyl having 1-20 C atoms, saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms, which may be substituted by alkyl groups having 1-6 C atoms, where one or more substituents R may be partially or fully substituted by halogen or partially by CN or NO₂ and halogen denotes F, Cl, Br or I, where up to four substituents R may be bonded to one another in pairs by a single or double bond and where a carbon atom or two non-adjacent carbon atoms of one or more substituents R may be replaced by atoms and/or atom groups selected from the group -O-, -C(O)-, -C(O)O-, -S-, -S(O)-, -SO₂-, -SO₃-, -N=, -N=N-, -NH-, -NR'-, -PR'-, -P(O)R'-, -P(O)R'-O-, -O-P(O)R'-O-, and -P(R')₂=N-, where R' denotes non-fluorinated, partially or perfluorinated alkyl having 1-6 C atoms, saturated or partially unsaturated cycloalkyl having 3-7 C atoms, unsubstituted or substituted phenyl or an unsubstituted or substituted heterocycle, X denotes F, Cl or Br, with the proviso that all four substituents R are not simultaneously hydrogen and

A⁻ is selected from the group
 [R¹OSO₃]⁻, [R¹SO₃]⁻, [R^FSO₃]⁻, [(FSO₂)₂N]⁻, [(R^FSO₂)₂N]⁻, [(R^FSO₂)(R^FCO)N]⁻, [(R^FSO₂)₃C]⁻, [(FSO₂)₃C]⁻, [R¹CH₂C(O)O]⁻, [R^FC(O)O]⁻, [P(C_nF_{2n+1-m}H_m)_yF_{6-y}]⁻, [P(C₆F₅)_yF_{6-y}]⁻, [(R¹O)₂P(O)O]⁻, [R¹₂P(O)O]⁻, [R¹P(O)O₂]²⁻, [R^F₂P(O)O]⁻, [R^FP(O)O₂]²⁻, [BF_{4-z}R^F_z]⁻,

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$[\text{BF}_{4-z}(\text{CN})_z]^-$, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $[\text{B}(\text{OR}^1)_4]^-$, $[\text{N}(\text{CN})_2]^-$, $[(\text{CN}_3)\text{C}]^-$, $[\text{N}(\text{CF}_3)_2]^-$,
 $[\text{HSO}_4]^-$, $[\text{SiF}_6]^{2-}$, $[\text{ClO}_4]^-$, $[\text{SCN}]^-$ and $[\text{NO}_3]^-$,

where $[\text{CF}_3\text{SO}_3]^-$ is excepted and

in which the substituents R^F in each case, independently of one another,

5

have the meaning of

perfluorinated and straight-chain or branched alkyl having 1-20 C atoms,

perfluorinated and straight-chain or branched alkenyl having 2-20 C

atoms and one or more double bonds,

perfluorinated and saturated, partially or fully unsaturated cycloalkyl

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having 3-7 C atoms, which may be substituted by perfluoroalkyl groups,

where the substituents R^F may be bonded to one another in pairs by a

single or double bond and

where a carbon atom or two non-adjacent carbon atoms of the substitu-

ent R^F which are not in the α -position to the heteroatom may be replaced

15

by atoms and/or atom groups selected from the group -O-, -C(O)-, -S-,

-S(O)-, -SO₂-, -N=, -N=N-, -NR'-, -PR'- and -P(O)R'-, where R' denotes

non-fluorinated, partially or perfluorinated alkyl having 1-6 C atoms,

saturated or partially unsaturated cycloalkyl having 3-7 C atoms,

unsubstituted or substituted phenyl or an unsubstituted or substituted

20

heterocycle,

in which the substituents R^1 in each case, independently of one another,

have the meaning of

straight-chain or branched alkyl having 1-20 C atoms,

25

straight-chain or branched alkenyl having 2-20 C atoms and one or more
double bonds,

straight-chain or branched alkynyl having 2-20 C atoms and one or more
triple bonds,

saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms,

30

which may be substituted by alkyl groups having 1-6 C atoms,

where the substituents R^1 may be partially substituted by CN, NO_2 or halogen and

halogen denotes F, Cl, Br or I,

where the substituents R^1 may be bonded to one another in pairs by a single or double bond and

where a carbon atom or two non-adjacent carbon atoms of the substituent R^1 which are not in the α -position to the heteroatom may be replaced by atoms and/or atom groups selected from the group -O-, -C(O)-, -C(O)O-, -S-, -S(O)-, -SO₂-, -SO₃-, -N=, -N=N-, -NH-, -NR'-, -PR'-, -P(O)R'-, P(O)R'O-, OP(O)R'O-, -PR'₂=N-, -C(O)NH-, -C(O)NR'-, -SO₂NH- or -SO₂NR'-, where R' denotes non-fluorinated, partially or perfluorinated alkyl having 1-6 C atoms, saturated or partially unsaturated cycloalkyl having 3-7 C atoms, unsubstituted or substituted phenyl or an unsubstituted or substituted heterocycle

and the variables

n denotes 1 to 20,

m denotes 0, 1, 2 or 3,

y denotes 1, 2, 3 or 4 and

z denotes 1, 2, 3 or 4.

17. Compounds according to Claim 16, characterised in that the substituents R denote hydrogen or a straight-chain or branched alkyl group having 1-12 C atoms,

with the proviso that all four substituents R are not hydrogen or at least two substituents R are bonded to one another by single or double bonds in such a way that a monocyclic cation is formed and

the counteranion A^- denotes

$[CH_3OSO_3]^-$, $[C_2H_5OSO_3]^-$, $[C(CN)_3]^-$,

$[CH_3SO_3]^-$, $[C_8H_{17}SO_3]^-$, $[CH_3C_6H_4SO_3]^-$, $[CF_3SO_3]^-$, $[C_2H_5SO_3]^-$,

$[CF_3CF_2SO_3]^-$, $[(CF_3SO_2)_2N]^-$, $[(FSO_2)_2N]^-$, $[(CF_3SO_2)(CF_3CO)N]^-$,

$[(C_2F_5SO_2)(CF_3CO)N]^-$, $[(C_2F_5SO_2)_2N]^-$, $[(CF_3SO_2)_3C]^-$, $[(C_2F_5SO_2)_3C]^-$,

5 [(FSO₂)₃C]⁻, [CH₃C(O)O]⁻, [C₂H₅C(O)O]⁻, [CF₃C(O)O]⁻,
[CF₃CF₂C(O)O]⁻, [PF₆]⁻, [P(C₂F₅)₃F₃]⁻, [P(C₄F₉)₃F₃]⁻, [P(CF₃)₃F₃]⁻,
[P(C₂F₄H)(CF₃)₂F₃]⁻, [P(C₂F₃H₂)₃F₃]⁻, [P(C₂F₅)(CF₃)₂F₃]⁻, [P(C₆F₅)₃F₃]⁻,
[P(C₃F₇)₃F₃]⁻, [P(C₂F₅)₂F₄]⁻, [(HO)₂P(O)O]⁻, [(CH₃O)₂P(O)O]⁻,
10 [(C₂H₅O)₂P(O)O]⁻, [(C₂F₅)₂P(O)O]⁻, [(C₂F₅)P(O)O₂]²⁻, [P(C₆F₅)₂F₄]⁻,
[(CH₃)₂P(O)O]⁻, [CH₃P(O)O₂]²⁻, [(CF₃)₂P(O)O]⁻, [CF₃P(O)O₂]²⁻, [BF₄]⁻,
[BF₃(CF₃)]⁻, [BF₂(C₂F₅)₂]⁻, [BF₃(C₂F₅)]⁻, [BF₂(CF₃)₂]⁻, [B(C₂F₅)₄]⁻,
[BF₃(CN)]⁻, [BF₂(CN)₂]⁻, [B(CN)₄]⁻, [B(OCH₃)₄]⁻, [B(CF₃)₄]⁻,
[B(OCH₃)₂(OC₂H₅)₂]⁻, [B(O₂C₂H₄)₂]⁻, [B(O₂C₂H₂)₂]⁻, [B(O₂C₆H₄)₂]⁻,
15 [N(CN)₂]⁻, [N(CF₃)₂]⁻, [HSO₄]⁻, [ClO₄]⁻, [SiF₆]⁻, [SCN]⁻ or [NO₃]⁻.

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